Bioavailability Considerations in Aquatic Bioaccumulation Assessment of Hydrocarbons

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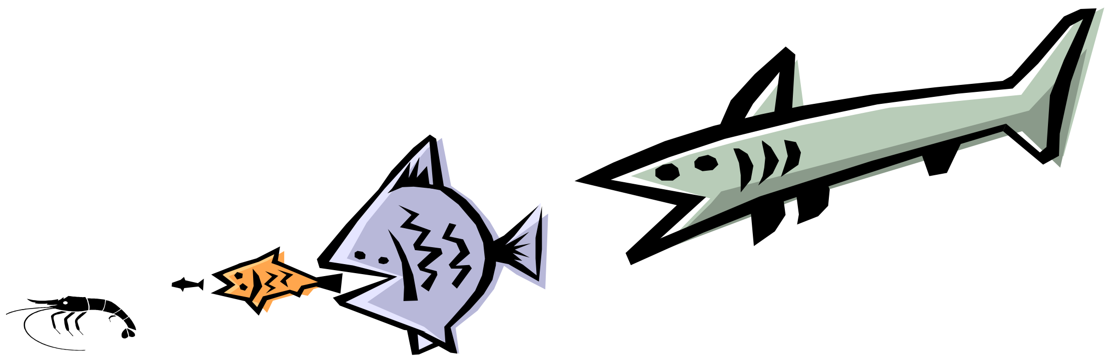
Introduction

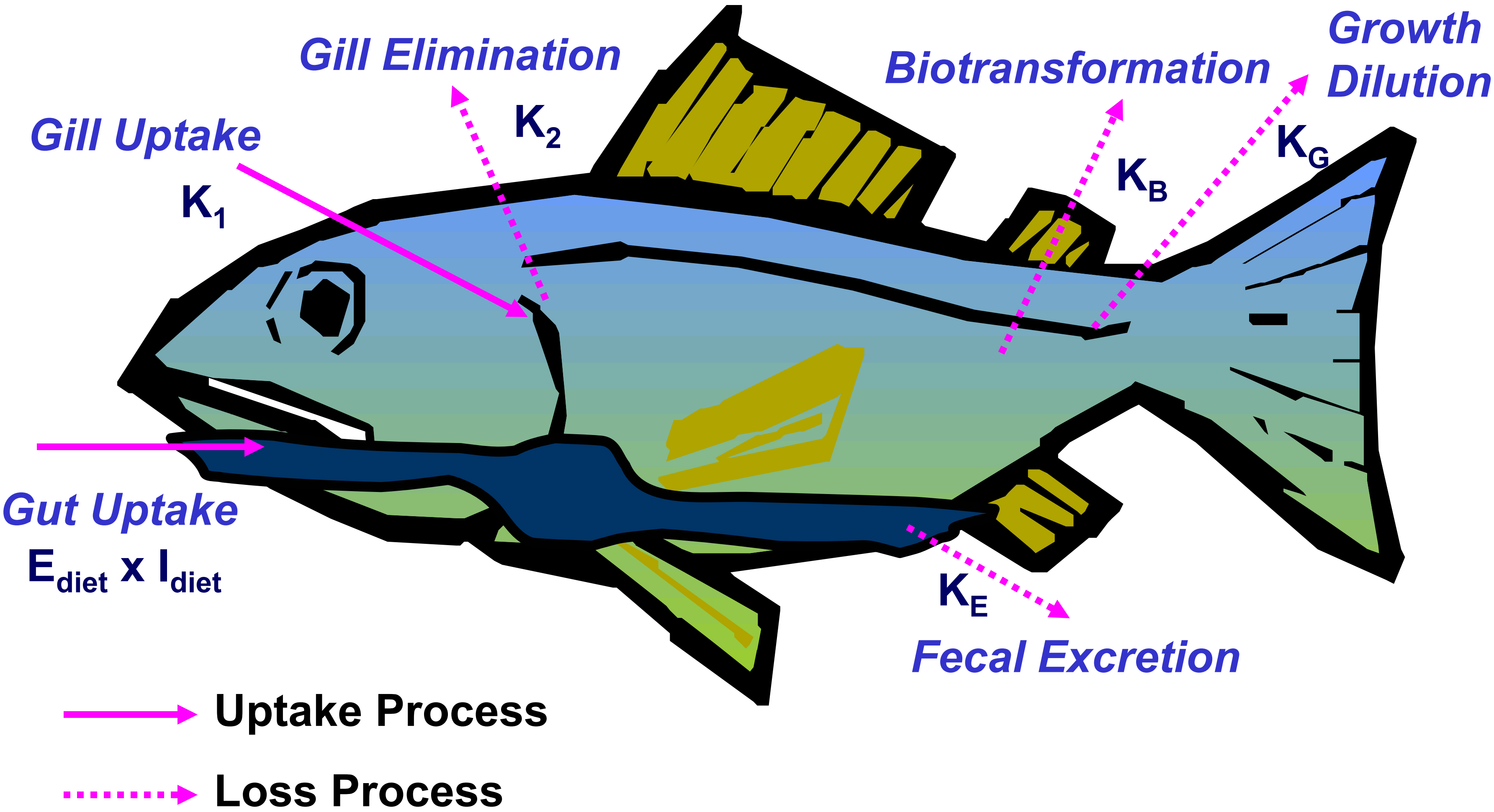
- **Bioavailability:**
  - **Extent to which human & ecological receptors are exposed**
  - **In the aquatic environment ... bioaccumulation in the foodchain often dictates contaminant exposure to upper trophic level biota**
    - **Bioaccumulation provides a measure of bioavailability**



- **Bioaccumulation potential in fish .. key regulatory concern:**
  - **PBT prioritization initiatives, e.g. categorization of Canadian DSL**
  - **Regional / site-specific risk assessment**
    - **Bioaccumulation often assessed using very simplistic models**

$$\text{Log BCF} = a + b \text{ Log } K_{ow}$$

Bioaccumulation Processes in Fish



Uptake Processes

- For neutral organics with Log K_{ow} > 3
  - Gill uptake controlled by:
    - Gill ventillation (depends on fish size)
    - Complexation to dissolved or particulate organic carbon
      - Reduces bioavailability
      - Bioavailable fraction = $1/[1+0.35K_{ow}\{POC\}+0.035K_{ow}\{DOC\}]$
  - Gut uptake depends on:
    - Ingestion rate of food
    - Assimilation efficiency of chemical from diet
      - Empirically related to Log K_{ow}
      - Role of metabolism in gut ignored in default models

Loss Processes

- **Gill Elimination:**

$$K_2 \text{ (1/day)} = K_1 / (L_{fish} K_{ow})$$

- **Gut Excretion:**

$$K_E \text{ (1/day)} = 0.2\, E_{diet}\, I_{diet}\, L_{diet} / L_{fish}$$

- **Growth-Dilution:**

$$K_G \text{ (1/day)} = 0.01\, W^{-0.2}$$

- **Biotransformation: Usually Ignored**

$$K_B \text{ (1/day)} = 0$$

L_{fish} = Lipid fraction in fish
L_{diet} = Lipid fraction in diet
W = Fish wet weight (g)

Quantifying Bioaccumulation

- **Aqueous Exposure:**

$$BCF = C_{fish} / C_{water} = K_1 / (K_2 + K_E + K_G)$$

- **Dietary Exposure:**

$$BMF = C_{fish} / C_{diet} = E_{diet}\, I_{diet} / (K_2 + K_E + K_G)$$

Express both parameters on lipid-normalized basis

Are Default Predictions Reliable for Hydrocarbons?

- **Experimental Data Needed .... However, limitations of BCF Test (e.g. OECD 305 Guideline)**
  - Constant aqueous concentrations often difficult to maintain
    - biodegradable, volatile nature
  - Analytical sensitivity may not be adequate
    - low water solubility, biotransformation in fish
  - Uncertainty regarding “bioavailability” of aqueous concentration complicates test interpretation
    - complexation to uneaten food / dissolved organic carbon
    - emulsion formation above true solubility
  - Expensive / Animal use intensive

Dietary Bioaccumulation Test

- **Overcomes problems associated with BCF test:**
  - **Allows higher / constant test exposures**
  - **Improves analytical detection of parent hydrocarbon**

- **Provides additional advantages:**
  - **Enables biomagnification via gut to be characterized**
  - **Reduces number of fish required**
  - **Saves considerable cost (50-75%)**

- **Promising alternative test for bioaccumulation assessment**

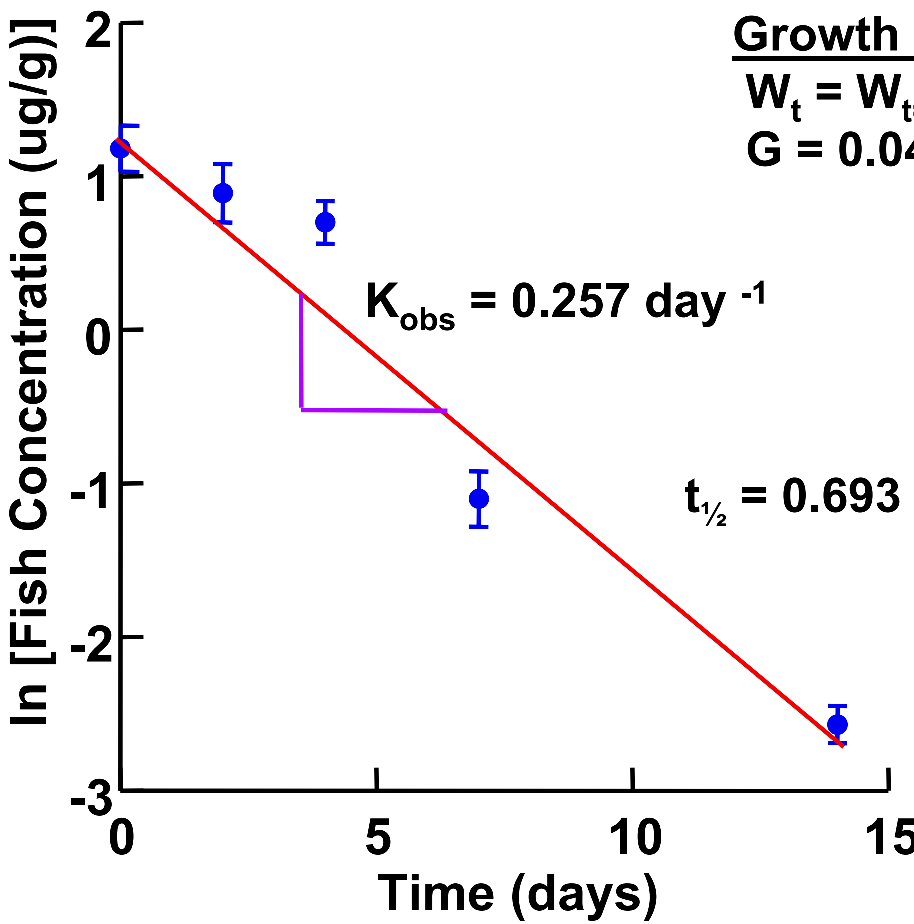
Experimental Approach

- Spike substance to commercial fish diet (14% lipid)
- Confirm dietary concentration analytically
- Feed 3% ration of spiked diet to trout (1-5 grams; 2-4% lipid) for 7 to 10 days (uptake)
- Transfer exposed fish to clean food (depuration)
- Analyze fish at different depuration times
  e.g. 0, 1, 2, 4, 7, 14 days

Data Analysis

- Use experimental depuration data to deduce:
  - Growth-corrected first-order half-life ($t_{½}$)
    i.e. $t_{½} = 0.693/K_{obs} = K_2 + K_E + K_B$
  - Assimilation efficiency from the diet (E_{diet})
- Use toxicokinetic parameters to calculate:
  - Biomagnification Factor (BMF)
  - Bioconcentration Factor (BCF)
    - Assume {DOC} in lab water = 2 mg/L

Example - 1,3,5 Trimethylcyclohexane Depuration



Growth During Test:

$W_t = W_{t=0}\, e^{Gt}$

G = 0.049 day $^{-1}$

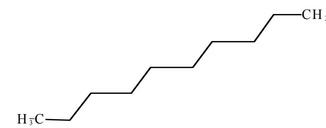
$t_{½}$ = 0.693 / 0.208 = 3.3 days

Testing Strategy

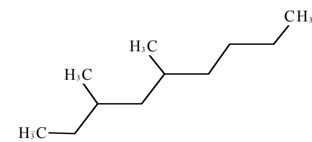
- **Test hydrocarbons with different structures & K_{ow}s from the classes:**

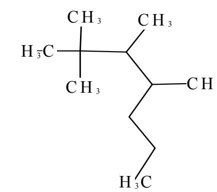
Aliphatics

- ➢ **P = Paraffins ... Linear Alkanes**

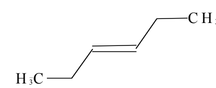


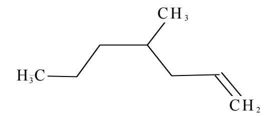
- ➢ **Isoparaffins ... Branched Alkanes**

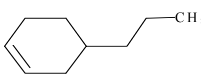




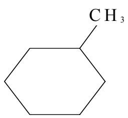
- ➢ **O = Olefins ... Alkenes**

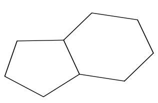


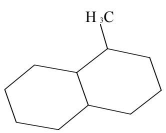




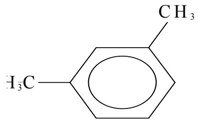
- ➢ **N = Naphthenes ... Cycloalkanes**

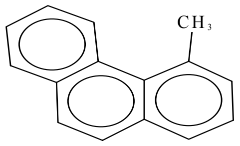


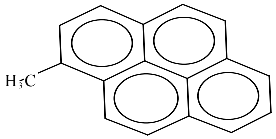




- ➢ **A = Aromatics ... Mono, Di & Poly**

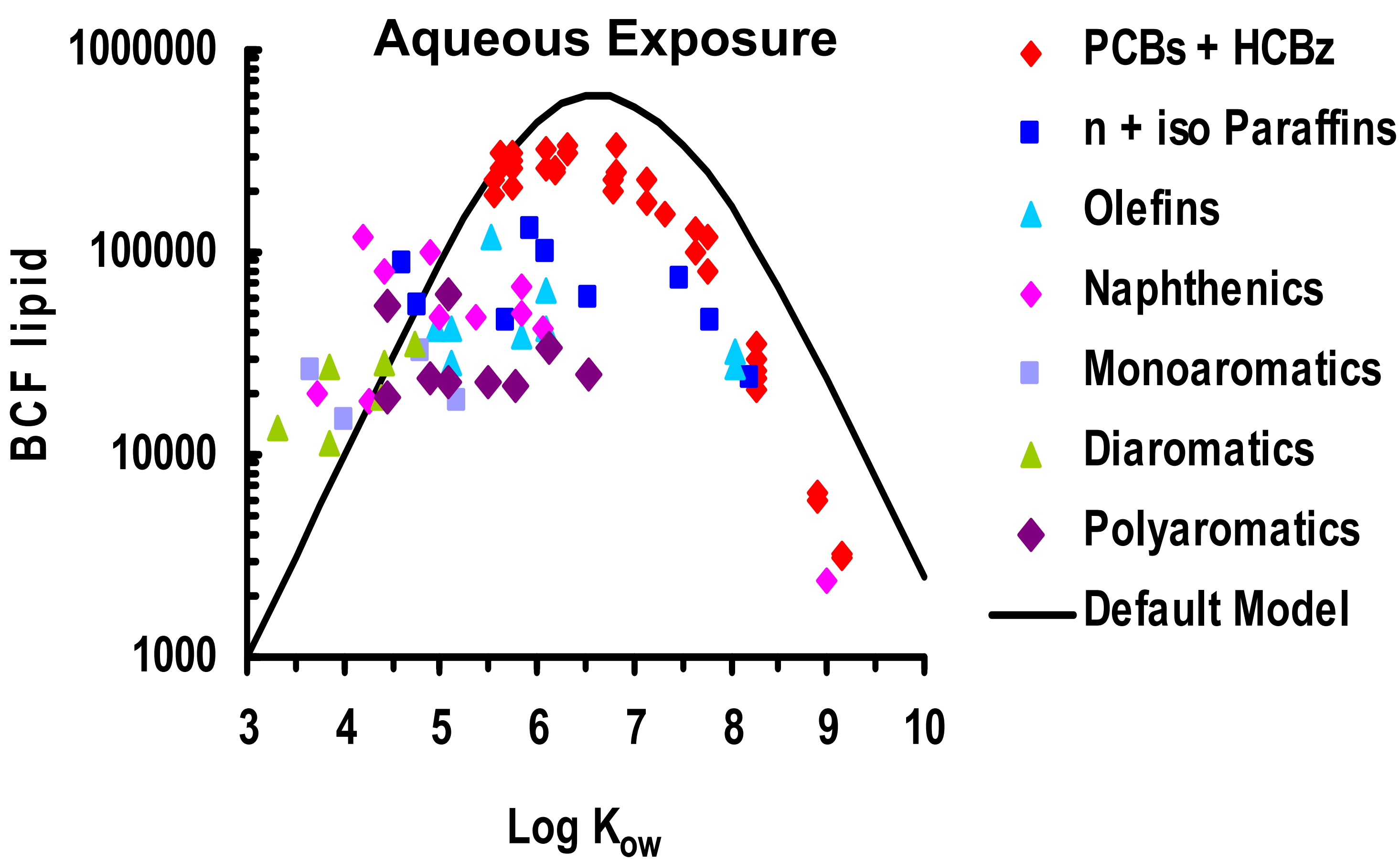






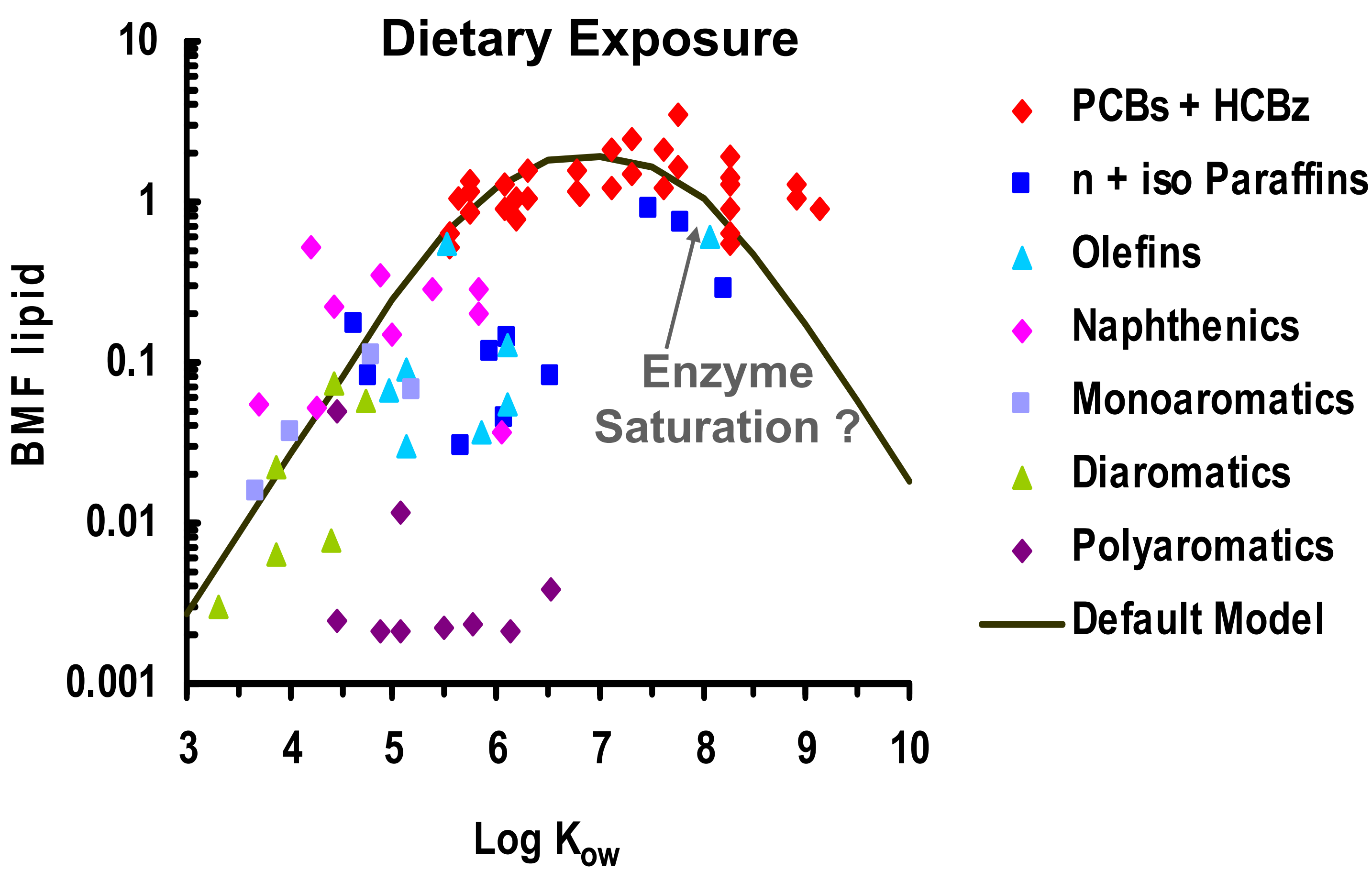
- ➢ **Hexachlorobenzene ... used as a positive control**

Comparison of Experimental BCF to Model



PCB Data Source: Fisk et al. (1998)

Comparison of Experimental BMF to Model



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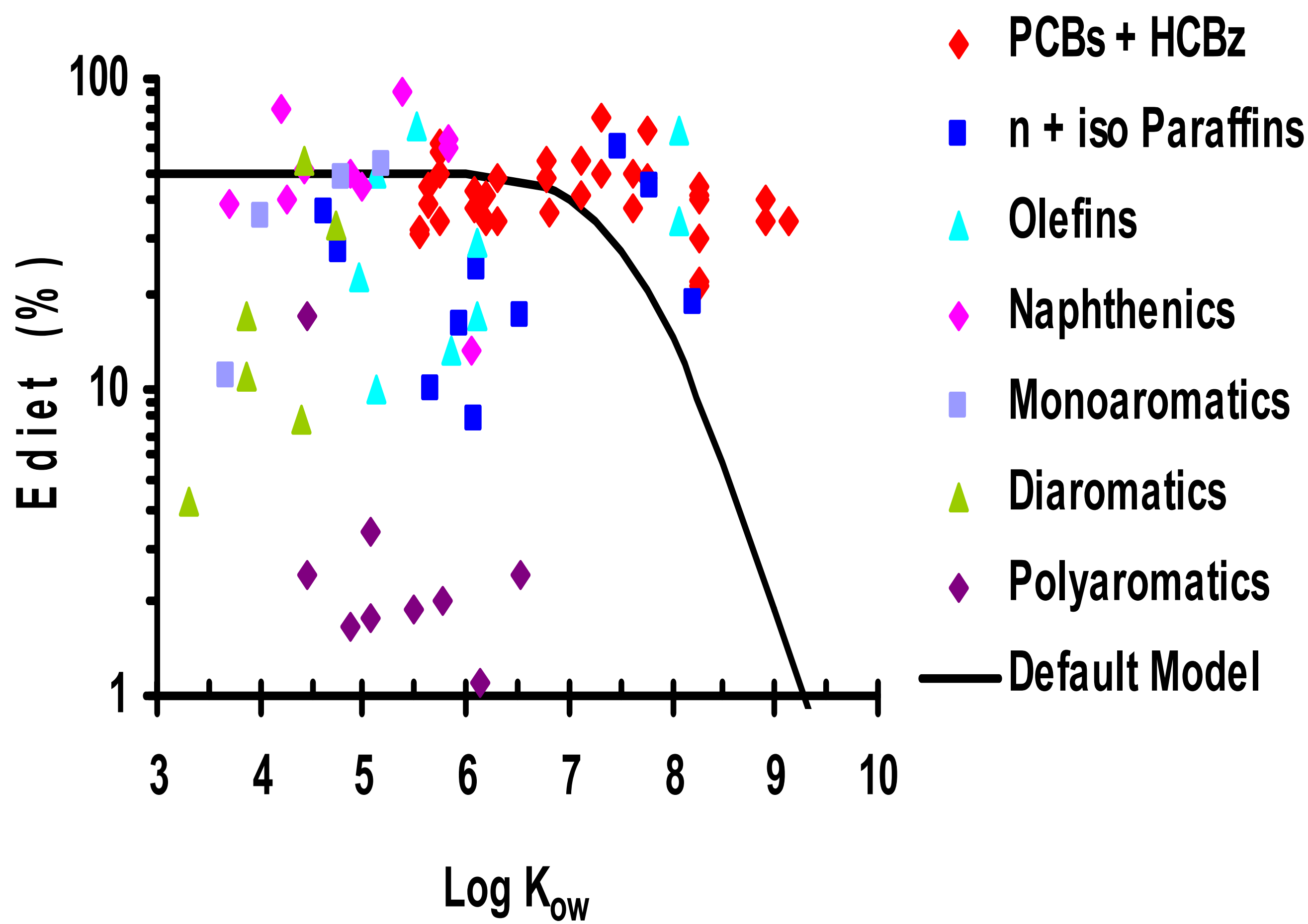
Assimilation Efficiency from the Diet



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Summary

- Simple linear BCF correlations with Log K_{ow} not reliable for predicting bioaccumulation potential in fish ... Ignores
  - Aqueous "Bioavailability"
  - Growth-Dilution
  - Biotransformation

- Process-based toxicokinetic models provide an improved mechanistic basis to predict bioaccumulation

- Toxicokinetic parameters can be derived via cost-effective dietary bioaccumulation test
  - Biotransformation in fish tissue and degradation in gut can significantly reduce hydrocarbon exposure via fish pathway
  - Experimental data form basis for improved QSARs
  - Potential extrapolation to terrestrial foodchain pathway ???
    - Correlation of Fish BMF with Cow BMF